REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-06-0076

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT .
	MARCH 2006	FINAL

4. TITLE AND SUBTITLE	5. FUNDING NUMBERS
POTENTIAL ENERGY SURFACES AND DYNAMICS OF HIGH ENERGY MATERIALS	F49620-02-1-0165

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
IOWA STATE UNIVERSITY AMES, IA 50011	

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSORING/MONITORING AGENCY REPORT NUMBER
AFOSR/NL 875 N. RANDOLPH STREET ARLINGTON, VA 22203 *Dr. Michael Berman*	

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT	12b. DISTRIBUTION CODE
APPROVE FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED	

13. ABSTRACT *(Maximum 200 words)*

14. SUBJECT TERMS

15. NUMBER OF PAGES 16

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UnClas	UnClas	UnClas	UnClas

1. COVER SHEET

AFOSR PROGRESS REPORT

POTENTIAL ENERGY SURFACES AND DYNAMICS OF HIGH ENERGY MATERIALS

REPORTING PERIOD 10/1/01 – 8/31/05

AFOSR F49620-02-1-0165

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20060323061

2. Objectives: No Change in Objectives

3. Status of effort: A brief statement of progress towards achieving the research objectives. (Limit to 200 words.)

On the theoretical side, a new highly scalable code for multi-configurational self-consistent field (MCSCF) calculations has been developed. This code is in the latest GAMESS release. A parallel code for second order unrestricted open shell perturbation theory (UMP2) gradients has been developed. The derivation for the Z-averaged open shell second order perturbation theory gradients has been completed, and a paper describing this derivation has been published. The parallel code for this method has now been completed. A new second order multi-reference perturbation theory (based on the generalized Van Vleck perturbation theory), GVVPT2 has been implemented in GAMESS. A preliminary code for the GVVPT2 gradients has been written, and a more robust code is in progress. The MCSCF analytic Hessian code has now been completed. Initial scaling tests suggest that this code, now available in GAMESS, will scale very well with the number of processors. A review paper on second order perturbation theory gradients has been published. A new, very effective coarse-grained parallel method, called GDDI, has been developed and implemented. This method has already proved to be very effective for numerical gradient and Hessian calculations, since each energy or energy + gradient calculation is completely independent of each other. Other developments include the implementation of a new density functional theory (DFT)-based effective fragment potential (EFP) method, the development of molecular dynamics and Monte Carlo methods to facilitate the study of solvation and liquid behavior, and the development and implementation of several MCSCF-based approaches to spin-orbit coupling. With regard to applications, considerable progress has been made in our understanding of the mechanisms for formation of POSS (polyhedral oligomeric silsesquioxanes) and their titanium analogs. A paper on ionic liquids based on triazolium cation has been published. A second paper on tetrazolium has been submitted, and a paper on pentazolium cation is in draft form. All of these calculations have been performed at a reasonable level of electronic structure theory (MP2 and G2 for heats of formation). Studies of multiple ion pairs have been initiated using our effective fragment potential (EFP), followed by re-optimizations with MP2.

4. Accomplishments/New Findings: Describe research highlights, their significance to the field, their relationship to the original goals, their relevance to the AF's mission, and their potential applications to AF and civilian technology challenges.

A. THEORY/MODEL DEVELOPMENT

Parallel Developments. A highly scalable code for frozen core second order perturbation theory gradients for closed shell molecules has been developed and is on-line for general use at several MSRC systems. This new code uses the Distributed Data Interface (DDI)

so that the large arrays do not have to be replicated. This means that much larger molecules can be studied using geometries based on correlated wavefunctions. The code scales very well for as many as 512 nodes and has already been applied to several challenging compounds. The development of analogous codes for molecules with unpaired electrons, using both restricted and unrestricted wavefunctions has been completed. A general overview paper on second order perturbation theory derivatives has been published. A paper on a DDI implementation of the SCF method has also been published. Improved parallel MCSCF codes have been completed, and a distributed parallel full CI code has been implemented and a paper published. A scalable MCSCF Hessian code has been developed and implemented. The multi-reference perturbation theory code (MCQDPT) has now been implemented under DDI. The effective fragment potential (EFP) code has been made scalable under DDI. In an important related development, parallel GAMESS now runs on clusters of PCs and Macs (running Linux) and high end workstations. This is more challenging than self-contained massively parallel computers, since the overhead due to inter-node communications is more complex. This issue has been solved to some extent by using a Gigabit Ethernet switch with large data packets. We are also exploring alternative communications solutions, such as Myrinet, SCI, and Infiniband. These developments and their applications have been enhanced by the construction of a new 32-node, 128-CPU IBM Power3+ cluster using funds provided by a DURIP grant. As for all other GAMESS developments, we will make our experiences in developing scalable clusters available to all users.

Condensed Phase Methods. We have already shown that our effective fragment potential (EFP) method for solvation is excellent for water, in a variety of applications. We are now working on extending the capabilities of the method in several ways. We are exploring several alternative approaches for incorporating dispersion and other higher order terms into the method. Such terms are particularly important for nonpolar solvents. We are also in the process of extending the model so that it is equally applicable and more slowly but accurate for any solvent. Key to the success is the derivation and implementation of general expressions for charge transfer and dispersion contributions that contain no fitted parameters. Now that these new terms have been implemented, an EFP can be generated for essentially any species, in particular ionic liquids. A paper on the dispersion term has been published, and a paper on the charge transfer term has just been accepted. The derivation of an expression for the analytic gradient for the EFP-*ab* initio interaction term is in progress. A very important new development (by co-worker Jan Jensen) is a new method for using EFPs across covalent bonds. This will facilitate the representation of large substituents, as well as the treatment of large biological molecules. We have also interfaced the EFP method with two continuum methods; the simple Onsager reaction field and the more sophisticated polarizable continuum model (PCM).

As the number of solvent molecules in the system increases, the number of configurations to be considered increases rapidly, and traditional small molecule geometry optimization methods are not effective. We are therefore developing both molecular dynamics and Monte Carlo simulation codes so that the configurational space can be probed more effectively, not only for minima, but for transition states and reaction paths as well. This is also an important first step in the development of methods based on the EFP model for

this is a very efficient approach, its accuracy is limited. However, there is an intermediate method, in which only those matrix elements connecting orbitals in the active space with each other are neglected. We have shown that in this case excellent agreement with the all electron method is obtained, without any need for fitted parameters. We have also implemented the RESC (relativistic elimination of the small component) method for calculating spin-orbit coupling interactions, complete with analytic gradients.

The other source of non-adiabatic interactions is derivative (vibronic coupling). We have now derived and implemented analytic CASSCF Hessians (energy second derivatives), and the analogous derivative coupling terms have been derived and coded. This functionality will be essential for studying excited states where surface crossings are common.

Density functional theory (DFT) has become extraordinarily popular in recent years, because it has the same computational requirements as Hartree-Fock theory, but often has a level of accuracy that is comparable to second order perturbation theory. We have developed and implemented a gridless approach to DFT, by using the resolution of the identity to evaluate the complicated integrals. This procedure requires the use of auxiliary basis sets to resolve the identity. After extensive analysis of the convergence of several molecular properties as a function of basis set, we have recommended a series of auxiliary basis sets for use with the first row in the periodic table. The next step will be to extend this basis set development to heavier elements. We have also implemented a more traditional grid-based DFT method, including all of the most popular functionals.

Another approach that is very important for large molecules, especially molecules that contain heavier elements, is the effective core potential (ECP) method. This method replaces inner shell electrons by model potentials, making the calculations much more efficient. These potentials include relativistic corrections for the heavier elements. To make these calculations more useful, we have developed much more efficient methods for obtaining the first and second energy derivatives; that is, the gradients and hessians. The increase in speed is a factor of 5-10, and the method has been implemented to take advantage of parallel computers. Very recently, our collaborator Mariusz Klobukowski has implemented model core potentials (MCP) into GAMESS. Because MCPs have the correct nodal characteristics, they are more accurate for many properties, such as spin-orbit coupling matrix elements and relativistic effects for heavy elements.

As calculations on larger and larger species are made feasible by advances in parallel programs and other innovative algorithms, it becomes increasingly important to develop graphical methods for interpreting the results of complex calculations. This has led to the continuing development of MacMolPlt, a graphical interface for GAMESS. MacMolPlt provides the ability to visualize (and rotate in real time) orbitals, wavefunctions, electron densities and electrostatic potentials in two and three dimensions. We are now in the process of developing a GUI (graphical user interface) that will make the construction of large and complex species much easier.

We have also been exploring alternatives and extensions to the popular G2 and G3 methods developed by Pople and co-workers for the accurate prediction of such theormodynamic properties as heats of formation, ionization potentials and electron affinities. One limitation of these methods is that they are applicable only to species that are adequately described by single configuration wavefunctions. This eliminates many transition metal compounds, diradicals and most transition states. We have therefore initiated, in collaboration with the Radom group, the development of multi-reference analogs of the G2 and G3 methods. The multi-reference methods are based on CASSCF wavefunctions, instead of Hartree-Fock, followed by multi-reference perturbation theory (instead of MP2) and finally multi-reference CI. The initial paper describing this method has been published.

B. APPLICATIONS

POSS Compounds. Polyhedral oligomeric silsesquioxanes (POSS) have a wide variety of important applications, including lubricants and coatings. They are also resistant to extreme environments. Consequently, there is considerable interest in these species in industry, universities and Air Force Laboratories. We have therefore initiated a detailed study of POSS compounds, with primary emphasis on the mechanisms by which these species form, in both the gas phase, and in solution and the presence of catalysts. In the first series of calculations, we examined the three stepwise hydrolysis steps of trichlorosilane, followed by the condensation of the product trihydroxysilane. All four reactions are predicted to have large barrier heights in the gas phase, but the addition of just one extra water molecule is sufficient to reduce all barriers to zero or nearly zero, except for the first hydrolysis step. In the latter, there is still a residual barrier of almost 10 kcal/mol. So, the next step will be to examine the effect of additional water molecules, especially on this first step.

Calculations have also been completed on the next steps in the mechanism, in which the initial condensation products, disiloxanes, are further condensed to the ring compounds D3 and D4. These results are consistent with those reported above, in that initially high barriers are reduced to nearly zero by an additional water molecule. The most recent effort has been the study of the addition of more water molecules, which lower barriers even further, and analysis of substituent effects on the reaction mechanism and energetics. Most recently, we have completed the first systematic study of the competing mechanisms for the entire formation of a POSS, T_8, from the starting siloxanes. This work has now been published.

Although our main focus is on Si-based POSS, the Ti analogs are also of interest. We have therefore initiated a series of calculations on the Ti-POSS compounds to study their properties. The first paper on mixed Si-Ti POSS has been published. These mixed Si-Ti POSS also have potential as catalysts, and a paper of the efficacy of these potential catalysts has been published.

Three dimensional cage compounds, including zeolites, have been of interest as a possible means for separating small gas molecules. In collaboration with Dr. Shawn Phillips (AFRL-Edwards) we have therefore completed a series of calculations in which the potential energy surfaces for passing N_2 and O_2 through the faces of T_n, n = 8, 10, 12. For T_8, both the energy barriers and the endothermicities are very large for both N_2 and O_2. In both cases, electron correlation is essential for an adequate estimate of the energetics. For N_2, the barrier height is on the same order as the SiO bond strength, while the O_2 barrier is much smaller. Despite these observations, the SiO bond does not break upon entry of either molecule, and the species with the gas molecules are minima on their respective potential energy surfaces. As the size of the cages increases, the barriers and endothermicities decrease as one would expect. A paper on this study has been published. We are now exploring similar possibilities for storing H_2 in POSS cages. Preliminary calculations on T_8 and its Ti and Zr analogs suggest that it is easier to insert H_2 into these cages, but there are still substantial energy barriers.

Fuels with High N-Content. There has been considerable interest in the last several years in the potential for cubic molecules as high energy fuels. Cubane itself has been considered, and so far rejected because of the complexity of its synthesis. The octasila analog of cubane has been prepared. Unlike the carbon system, the cubic structure is the most stable Si_8H_8 isomer. This makes it potentially very interesting, since it is still rather high in energy. However, the heavy mass of Si precludes any viability of such species as high energy fuels.

On the other hand, cubic N_8 is a light, very high energy fuel that has been the subject of considerable attention. Extensive calculations, however, illustrate that the upper limit of the barrier separating this species from four nitrogen molecules is 20 kcal/mol. It is, therefore, not a viable high energy fuel. In the process of studying the cubic N_8 potential energy surface, it was discovered that there are three N_8 isomers that are much lower in energy than the cube, yet still much higher in energy than molecular nitrogen. The potential energy surfaces for these isomers have now been studied in detail. Two of these have barriers on the order of 15-20 kcal/mol (too small), but the third has a barrier of nearly 30 kcal/mol. So, this isomer may be a viable synthetic target.

Related to the foregoing, much attention has been paid recently to N_4 as a potential fuel. Many references are made to a barrier on the order of 50-65 kcal/mol, even though it has been shown by Yarkony that non-adiabatic interactions reduce this barrier to less than 40 kcal/mol. For the first time, we have mapped out the potential energy surface that leads from tetrahedral N_4, using second order perturbation theory. One also must consider the possibility that two N_4 molecules could interact and form molecular nitrogen. This possibility is being explored in this laboratory.

Rob Schmitt at SRI proposed an intriguing series of potential high energy compounds that we have been exploring computationally. The procedure is to use a modified version of G2 to predict the heats of formation and then to use these predictions to assess the specific impulse. For the most promising species, further studies are performed in which

the stability of these compounds with respect to unimolecular decomposition, bimolecular interactions and attack by environmental species such as water.

Christe and co-workers at AFRL (Edwards) have isolated the first new all-nitrogen species in nearly a century. With the counter ion, this species is $[AsF_6^-][N_5^+]$. We have now studied the potential energy surface of this species as it forms $AsF_5 + FN_5$, and subsequently the pathway leading from FN_5 to $FN_3 + N_2$. A paper describing this work has recently been published. Another paper on the possibility of making crystals of N_5^+/N_5^-, has been published. Both of these latter papers have been done in collaboration with colleagues at AFRL-Edwards.

Cryogenics. There has been considerable experimental and theoretical interest in metal-doped solid hydrogen. We have an ongoing series of investigations of the low-lying electronic states of BH_2 system, to determine the energetics by which the metal is held as a weakly bound species in the matrix and the ease with which two metal atoms find each other. Similar studies are under way on the B_2-H_2 system and the Al analogs.

The desired reaction product for burning Al-doped H_2 is Al_2O_3, since it is the thermodynamically most stable aluminum oxide. However, it is unknown how or when this species forms in the process. We have therefore initiated an extensive study of the potential energy surface that leads from Al and O_2 to various oxides. A paper on the reaction of Al with O_2 to from AlO_2, and the subsequent formation of Al_2O_3 has now been published.

Ionic Liquids. A major effort in the study of ionic liquids has been initiated. Computations on the electronic structures of substituted triazolium, tetrazolium and pentazolium cations are ongoing, in an attempt to assess which substituents best stabilize these cations and enhance desirable properties. Heats of formation of these substituted cations have been predicted using G2 theory and isodesmic reactions. Calculations on each of these cations paired with NO_2^-, ClO_4^-, and dinitramide have also been performed. These calculations suggest than a single pair of ions frequently undergoes a barrier-less proton transfer to form a neutral pair, although a small number of stable ion pairs has been found. This suggests that one needs to increase the number of dimer pairs, approaching a unit cell and ultimately the bulk. This can be accomplished using the new EFP2 method, now that dispersion and charge transfer terms have been derived and implemented. We are now in the process of using the EFP2 method to predict structures and energetics for multiple ion pairs. For small systems, the geometries will be re-optimized using MP2, so that the EFP2 method can be carefully calibrated. For larger systems and for simulating bulk properties, the EFP2 method will be used on its own.

5. <u>Personnel Supported</u>: List professional personnel (Faculty, Post-Docs, Graduate Students, etc.) supported by and/or associated with the research effort.

Dr. Michael W. Schmidt, Senior Research Associate

Dr. Brett Bode, graduate student, postdoctoral research associate
Professor Larry Burggraf
Dr. Cheol Ho Choi, postdoctoral research associate
Professor Gyusung Chung
Dr. Tim Dudley, postdoctoral associate
Ms. Sherrie Elzey, undergraduate student
Mr. Dmitri Fedorov, graduate student.
Mr. Mark Freitag, graduate student.
Dr. Kurt Glaesemann, graduate student, postdoctoral research associate
Ms. Vassiliki-Alexandra Glezakou, graduate student.
Professor Takako Kudo, Gunma University.
Dr. Grant Merrill, postdoctoral research associate.
Ms. Heather Netzloff, graduate student
Mr. Michael Pak, graduate student.
Ms. Sanja Pudar, undergraduate student
Professor Leo Radom, Australian National University.
Dr. Michael Schmidt
Major James Shoemaker
Ms. Debbie Zorn, graduate student
Dr. Hui Li, postdoctoral research associate

6. <u>Publications</u>: List peer-reviewed publications submitted and/or
accepted during the 12-month period starting the previous 1 October (or since
start for new contracts).

1. M.S. Gordon, M.A. Freitag, P.Bandyopadhyay, V. Kairys, J.H. Jensen, and W.J.
Stevens, "The Effective Fragment Potential Method: A QM-Based MM Approach to
Modelling Environmental Effects in Chemistry", J. Phys. Chem. (Feature Article), 105,
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2. C.H. Choi, L. Ruedenberg and M.S. Gordon, "A new parallel optimial-parameter fast
multipole method", J. Comp. Chem., 22, 1484 (2001).

3. M.V. Pak and M.S. Gordon, "The Potential Energy Surfaces for AlO_2 using Multi-
reference Wave Functions", Chem. Phys. Lett., 344, 236(2001).

4. T.I. Solling, D.M. Smith, L. Radom, M.A. Freitag, and M.S. Gordon, "Multi-reference
equivalents of the G2 and G3 methods using reduced Moller-Plesset orders, J. Chem.
Phys., 115, 8758 (2001)..

5. "Gradient of the ZAPT2 Energy", G.D. Fletcher, M.S. Gordon and R.S. Bell, Theor.
Chem. Accts., 107, 57 (2002).

6. T. Kudo and M.S. Gordon, "Structures and Stabilities of Titanium Silsesquioxanes", J.
Phys. Chem. A, 105, 11276 (2001).

7. Y. Alexeev, R.A. Kendall and M.S. Gordon, "The Distributed Data SCF", Computer Physics Commun., 143, 69 (2002)

8. P. Bandyopadhyay, B. Mennucci, J. Tomasi, and M.S. Gordon "An Effective Fragment – Polarizable Continuum Approach to Solvation: Theory and Application to Glycine", J. Chem. Phys., 116, 5023 (2002).

9. T. Kudo and M.S. Gordon, "Exploring the Mechanism for the Synthesis of Silsesquioxanes. 3. The Effect of Substituents and Water", J. Phys. Chem., 106, 11347 (2002).

10. B. Tejerina and M.S. Gordon, "Insertion Mechanism of N_2 and O_2 into T_n (n = 8, 10, 12)-Silsesquioxane Framework", J. Phys. Chem., A106, 11764 (2002).

11. M.V. Pak and Mark S. Gordon, "Hyperfine coupling tensors for multi-configurational quasi-degenrate perturbation theory (MCQDPT)", J. Chem. Phys., 118, 40 (2003).

12. M.V. Pak and M.S. Gordon, "Potential energy surfaces for the Al + O_2 reaction", J. Chem. Phys., 118, 4471 (2003).

13. I. Adamovic, M.A. Freitag and M.S. Gordon, "Density Functional Theory Based Effective Fragment Potential", J. Chem. Phys., 118, 6725 (2003).

14. C. M. Aikens, S. P. Webb, R. Bell, G.D. Fletcher, M.W. Schmidt, and M.S. Gordon, "A derivation of the frozen-orbital unrestricted open shell and restricted closed shell MP2 analytic gradient expressions", Theor. Chem. Accts., 110, 233 (2003).

15. H.M. Netzloff, M.S. Gordon, K. Christe, A. Vij, V. Vij, and J.A. Boatz, "On the Existence of FN_5: A Theoretical and Experimental Study", J. Phys. Chem., 107, 6638 (2003).

16. T. Kudo and M.S. Gordon, "*Ab initio* Study of the Catalytic Reactivity of Titanosilsesquioxanes and Titanosiloxanes", J. Phys. Chem., A107, 8756 (2003).

17. D.G. Fedorov, R.M. Olson, K. Kitaura, M.S. Gordon, and S. Koseki, "A new hierarchical parallelization scheme: Generalized distributed data interface (GDDI), and an application to the fragment molecular orbital method (FMO)", J. Comp. Chem., 25, 872 (2004).

18. D. A. Dixon, D. Feller, K. O. Christe, W. W. Wilson,[‡] A. Vij, V. Vij, H. D. B. Jenkins, R. M. Olson, and M. S. Gordon, "Enthalpies of Formation of Gas Phase N_3, N_3^-, N_5^+, and N_5^- from *Ab Initio* Molecular Orbital Theory, Stability Predictions for $N_5^+N_3^-$ and $N_5^+N_5^-$, and Experimental Evidence for the Instability of $N_5^+N_3^-$", J. Am. Chem. Soc., 126, 834 (2003).

19. C.M. Aikens and M.S. Gordon, "Parallel Unrestricted MP2 Analytic Gradients using

the Distributed Data Interface", J. Phys. Chem., <u>108</u>, 3103 (2004).

20. H. Netzloff and M.S. Gordon, "The Effective Fragment Potential: Small Clusters and Radial Distribution Function", J. Chem. Phys., <u>121</u>, 2711 (2004).

21. T.J. Dudley, M.W. Schmidt, and M.S. Gordon, "Implementation and Parallelization of Analytic MCSCF Second Derivatives", J. Comp. Chem., in press

22. H. Netzloff and M.S. Gordon, "Fast Fragments: The Development of a Parallel Effective Fragment Potential Method", J. Comp. Chem., <u>25</u>, 1926 (2004)

23. I. Adamovic and M. S. Gordon, "Dynamic polarizability, dispersion coefficient C_6, and dispersion energy in the effective fragment potential method", Mol. Phys., <u>103</u>, 379 (2005).

24. M.S. Gordon and M.W. Schmidt, "Advances in Electronic Structure Theory: GAMESS a Decade Later", <u>Theory and Applications of Computational Chemistry</u>, Ch. 41, C. E. Dykstra, G. Frenking, K.S. Kim, G.E. Scuseria, Eds., Elsevier, 2005.

25. T. Kudo and M.S. Gordon, "Exploring the Mechanism for the Synthesis of Silsesquioxanes. 4. The Synthesis of T_8", J. Phys. Chem., <u>A109</u>, 5424 (2005).

26. T.J. Dudley and M.S. Gordon, "Theoretical Study of the Formation and Isomerization of Al_2H_2", Mol. Phys., in press.

27. Michael W. Schmidt, Mark S. Gordon, and Jerry A. Boatz, "Triazolium-Based Energetic Ionic Liquids", J. Phys. Chem., <u>A109</u>, 7285 (2005).

28. H. Li and M.S. Gordon, "Gradients of the Exchange-Repulsion Energy in the Effective Fragment Potential Method", Theor. Chem. Accts., in press.

29. D.Zorn, J.A. Boatz and M.S. Gordon, "Tetrazolium-Based Energetic Ionic Liquids", J. Phys. Chem., submitted.

7. <u>Interactions/Transitions:</u>

a. Participation/presentations at meetings, conferences, seminars, etc.

TALKS AT PROFESSIONAL MEETINGS

1. "Cluster Approaches to Solvation and Surface Chemistry", New Frontiers in Theoretical Chemistry, Tokyo, March 2001 (INVITED)

2. "Cluster Approaches to Solvation and Surface Chemistry" National ACS Meeting, San Diego, April 2001 (INVITED).

3. "New Advances in Scalable Computing", National ACS Meeting, San Diego, April 2001 (INVITED).

4. "Mechanisms for Formation of Polyhedral Oligomeric Silsesquioxanes", AFOSR Molecular Dynamics Contractors' Meeting, May 2001 (INVITED).

5. "Cluster Approaches to Surface Chemistry", National ACS Meeting, Chicago, August 2001 (INVITED).

6. "A Layered Approach to Solvation", National ACS Meeting, Chicago, August 2001 (INVITED)

7. "Cluster Approaches to Solvation and Surface Chemistry", Midwest Thoeretical Chemistry Conference, Minneapolis, MN, Oct. 2001 (INVITED).

8. "Recent Advances in Electron Correlation", National ACS Meeting, Orlando, April 2002 (INVITED)

9. "Tools for Exploring Potential Energy Surfaces", National ACS Meeting, Orlando, April 2002 (INVITED)

10. "A DFT-Based Effective Fragment Potential Method", National ACS Meeting, Orlando, April 2002, Ivana Adamovic presenting.

11. "*Ab Initio* and EFP-Based Molecular Dynamics", National ACS Meeting, Orlando, April 2002, Heather Netzloff presenting.

12. "*Ab Initio* – EFP Gradients", National ACS Meeting, Orlando, April 2002, Jamie Rintelman presenting.

13. "An Overview of the Effective Fragment Potential Method" Workshop on Time-Dependent Density Functikonal Theory (INVITED), Air Force Research Laboratory, May 2002

14. Theoretical Studies of Polynitrogen Compounds", Workshop on High Energy Species (INVITED), Lawrence Livermore National Laboratory, September 2002

15. "Tools for the Study of Ionic Liquids", Workshop on Ionic Liquids (INVITED), Washington, DC, October 2002

16. "Effective fragment potential method: From molecules to clusters to the bulk", National American Chemical Society Meeting, Philadelphia (INVITED), August 2004, H. Netzloff presenting.

17. "Treatment of dispersion energy in the general effective fragment potential

(EFP2) method", National American Chemical Society Meeting, Philadelphia, August 2004, I. Adamovic presenting.

18. "High Performance Electronic Structure Theory: Strategies and Applications", Seventh Congress of World Association of Theoretically Oriented Chemists", Capetown South Africa, Jan. 2005 (INVITED)

19. "Polyhedral Oligomeric Silsesquioxanes: Formation Mechanisms and Properties", American Physical Society National Meeting, March 2005, Los Angeles CA, INVITED

20. "Scalable Correlated Electronic Structure Methods: Straegies and Applications", Lise Meitner Symposium, June 2005, Jerusalem, Israel (INVITED)

21. "Scalable Correlated Electronic Structure Methods: Straegies and Applications", 1st Naregi Conference, June 2005, Nara, Japan (INVITED)

22. "Scalable Electronic Structure Theory: Strategies and Applications", National American Chemical Society (COMP), August 2005, INVITED

23. "Scalable Electronic Structure Theory: Strategies and Applications", National American Chemical Society (COMP), August 2005, INVITED

INVITED LECTURES

1. "Cluster Approaches to Solvation and Surface Chemistry", Gustavus Adolphus College, March 2001

2. "Cluster Approaches to Solvation and Surface Chemistry", St. Mary's College, April 2001

3. "Cluster Approaches to Solvation and Surface Chemistry", University of Southern California, April 2001

4. "Cluster Approaches to Solvation and Surface Chemistry", University of California-Irvine, May 2001

5. "Cluster Approaches to Solvation and Surface Chemistry", Australian national University, November 2001

6. "Cluster Approaches to Solvation and Surface Chemistry", Penn State University, February 2002

7. "Cluster Approaches to Solvation and Surface Chemistry", University of North Texas, May 2002

8. "Cluster Approaches to Solvation and Surface Chemistry", NASA-Ames Research Center, September 2002

9. "Cluster Approaches to Solvation and Surface Chemistry", Wright Laboratories Workshop on Time-Dependent Density Functional Theory, September 2002

10. "Potential Energy Surfaces for Polynitrogen Species", Workshop on Energetic Materials", Lawrence Livermore National Laboratory, September 2002.

11. "A Cluster-based Approach to Solvation", University of Western Australia, March 2003

12. "A Cluster-based Approach to Solvation", University of Tasmania, April 2003

13. "A Cluster-based Approach to Solvation", University of Melbourne, April 2003

14. "A Cluster-based Approach to Solvation", Australian National University, April 2003

15. "A Cluster-based Approach to Solvation", North Dakota State University, September 2003

16. "A Cluster-based Approach to Solvation", University of Wisconsin, April 2004

17. "A Cluster-based Approach to Solvation", Texas Tech University, October 2004

18. "A Cluster-based Approach to Solvation", Australian National University, November 2004

19. "A Cluster-based Approach to Surface Science", University of Melbourne, December 2004

20. "Effective Fragment Potentials: Solvation and Beyond", The Hebrew University, June 2005

21. "Effective Fragment Potentials: Solvation and Beyond", The Weizmann Institute, June 2005

b. Consultative and advisory functions to other laboratories and agencies, especially Air Force and other DoD laboratories. Provide factual information about the subject matter, institutions, locations, dates, and name(s) of principal individuals involved.

• Served as co-advisor to Major James Shoemaker, who received his Ph.D. from the Department of Engineering Physics, Air Force Institute of Technology, October 1997. Several papers from this work; are already in print.

• Collaborating with Dr. Jeff Bottaro (SRI) and Dr. Jerry Boatz (AFRL) to develop new HEDM compounds.

• Collaborating with Dr. Shawn Phillips (AFRL) to determine the mechanisms for the formation of POSS.

• Collaborating with Drs. Paul Day and Ruth Pachter (AFRL) to study the behavior of clusters of water and other solvents.

• Collaborating with Dr. Ruth Pachter to develop density-functional-based effective fragment potentials.

• Collaborating with Dr. Pachter and Dr. Nguyen (AFRL) to implement time-dependent DFT into GAMESS.

• Collaborating with Dr. Greg Drake, Dr. Tommy Hawkins and Dr. Jerry Boatz (AFRL) on the development of methods for treating ionic liquids.

c. Transitions. Describe cases where knowledge resulting from your effort is used, or will be used, in a technology application. Transitions can be to entities in the DOD, other federal agencies, or industry. Briefly list the enabling research, the laboratory or company, and an individual in that organization who made use of your research.

Both GAMESS and MacMolPlt have an increasing number of users in universities, industry, and government laboratories. The latest version of parallel GAMESS is on-line at all DoD Major Shared Resource Centers.

8. New discoveries, inventions, or patent disclosures. (If none, report None.) **None**

9. Honors/Awards: List honors and awards received during the grant/contract period. List lifetime achievement honors such as Nobel prize, honorary doctorates, and society fellowships prior to this effort.

¶ Named Fellow, American Physical Society, 2000

¶ Named Distinguished Professor of Chemistry, May, 1998

¶ Named to list of 100 most cited chemists, 1981-2000.

¶ Named 2004 recipient of ACS Midwest Award

¶ Elected to International Academy of Quantum Molecular Science (2004)

10. <u>Markings</u>: In order to ensure prompt receipt and acceptance,
mark the outside of the package clearly to indicate that it is a progress report.